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be chosen so that the coordinates of the focal points of a harmonic congruence are of the respective forms

$$\frac{\partial x}{\partial u}, \frac{\partial x}{\partial v}. \quad (19)$$

In this case equation (18) assumes the form (1), so that the choice of coordinates referred to its equivalent to finding a particular solution of (18).

Since the congruence F_1F_2 is harmonic to both N and N_1 , it follows that the equations of any transformation T in homogenous coordinates is reducible to the form (2). If the coordinates of N satisfy (18), the equations are of the form

$$\frac{\partial x_1}{\partial u} = h \frac{\partial}{\partial u} \left(\frac{x}{\theta} \right), \quad \frac{\partial x_1}{\partial v} = l \frac{\partial}{\partial v} \left(\frac{x}{\theta} \right), \quad (20)$$

where now θ is a solution of (18).

When the equations of the transformation are of the form (2), each solution of the point equation of N gives a new transform by means of (5). The equations of the preceding results continue to be true, and parallel nets are replaced by any transforms.

Although these results have been stated in terms of 3-space, they hold for two dimensional spreads in n -space, provided that a congruence is defined as a two parameter family of lines possessing two families of developables.

¹ Eisenhart, *Trans. Amer. Math. Soc.*, New York, **18**, 1917, (97-124).

² Bianchi, *Ann. Mat., Milano*, (Ser. 3), **11**, 1905, (93-158).

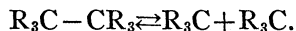
THE MOLECULAR WEIGHTS OF THE TRIARYLMETHYLS

By M. Gomberg and C. S. Schoepfle

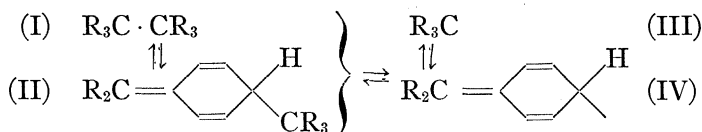
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Communicated May 31, 1917

It is now generally accepted that the free radicals of the triphenylmethane series owe their unique unsaturated character to the presence of a trivalent carbon atom in the molecule. In many cases the molecular weight has been found to be double that calculated for the free radical. Nevertheless, even in these cases the presence of a compound with a single unsaturated carbon atom is still recognized, and the assumption is made that there exists, in virtue of partial dissociation, a mobile equilibrium:



It is doubtful whether the matter is quite as simple as it is represented by the above equation. From a variety of experimental evidence¹ the conclusion seems inevitable that both the hexa-arylethanes and the triarylmethyls exist in two tautomeric modifications. It is far more likely that triarylmethyls, at least when in solution, conform to the following scheme:²



In other words, there is a tautomeric equilibrium between the benzenoid hexa-arylethane (I) and the quinol (II); also between the benzenoid triarylmethyl (III) wherein the central carbon atom is trivalent and its quinonoid modification (IV) wherein the *para*-carbon atom in the nucleus assumes the trivalent state. This viewpoint is in entire harmony with the peculiar chemical and physical behavior of this class of compounds. It permits us to explain, by the presence of the quinol tautomer (II), the existence of a colored modification of hexa-arylethanes in cases where molecular weight determinations fail to indicate an actually measurable degree of dissociation. And even in those cases where a partial or complete dissociation of the hexa-arylethane is demonstrable, the fact that the solution is colored finds a more reasonable and more concordant explanation in the existence of the quinonoid tautomeric triarylmethyl (IV) than merely in that of the benzenoid (III) alone.³

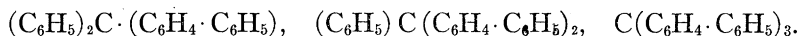
Whether, however, the supplemental hypothesis of tautomerism is accepted or not, the fact remains that we are dealing primarily with a phenomenon where a hydrocarbon dissociates spontaneously into two parts, which parts may, also spontaneously, reassociate with the production of the original substance. What are the factors which influence the degree of dissociation in a given hexa-arylethane? What is the relation between the degree of the dissociation and the nature of the aryl group in the substituted ethane?

Factors Influencing Dissociation.—Obviously, the nature of the solvent, the temperature of the solution, and the concentration of the solute must be the chief factors as regards the extent of dissociation which may be reached by a given hexa-arylethane. With regard to changes in the equilibrium between the dimolecular and the monomolecular modification due to the temperature, it has been found⁴ that the molecular weight of triphenylmethyl in naphthalene at 79°–80° is approximately 414, while the average value found with other solvents such

as benzene, nitrobenzene, etc. which freeze at temperatures around 0° – 5° , is between 480 and 485. A computation from these molecular weight determinations indicates that triphenylmethyl exists in the monomolecular state to an extent of 17% in naphthalene at 80° , while to considerably less than 5%, if at all, in benzene at 6° . Schlenk and Mair⁵ determined the molecular weight of triphenylmethyl in benzene by the ebullioscopic method, and found that at the temperature of the boiling point of benzene, also about 80° , the hydrocarbon is dissociated in the monomolecular phase to the extent of 23.3–29.9% with approximately a 2 % concentration. Schmidlin⁶ calls attention to the fact that it is very difficult to obtain an absolutely pure sample of triphenylmethyl and that samples prepared by slightly different methods often differ considerably in purity. Therefore he suggests the possibility that the variation between the molecular weights found by Schlenk with the ebullioscopic method and by Gomberg and Cone with the cryoscopic method may be due to differences in the degree of purity of the samples used. Accordingly, he constructed a special apparatus containing two thermometers, by means of which he could determine the molecular weight in benzene first by the ebullioscopic method and then by the cryoscopic method on one and the same sample. However, the molecular weights of triphenylmethyl found by the two methods showed no appreciable difference in value, and therefore no change in dissociation between the temperatures of 6° and 80° was noticeable.

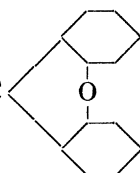
With regard to the influence of concentration upon the degree of dissociation of hexaphenylethane, an examination of the results obtained by various investigators fails to reveal a concordant influence of this factor. Neither molecular weight determinations nor the application of optical methods⁷ have supplied information of a sufficiently decisive nature to warrant us in drawing any conclusion as regards the concentration influences affecting the equilibrium between the dimolecular and the monomolecular triarylmethyl.

Relation Between Dissociation and the Nature of the Aryl Groups.—Although triphenylmethyl, the first and simplest representative of the triarylmethyls, was found to be largely in the dimolecular state, some of its analogs were found to exist to a large extent as monomolecular. Among the first triarylmethyls of this kind was the series containing *p*-biphenyl groups:

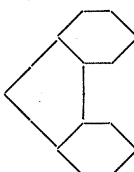


Schlenk and his co-workers concluded from the measurements of the molecular weight by the cryoscopic method with benzene as a solvent,

that these compounds are monomolecular to the extent of 15%, 80%, and 100%, respectively.⁸ From these results one might infer that the dissociation of the hexa-arylethane into free radicals is greatly favored by the complexity or the weight of the aryl groups,—the dissociation becoming apparently more manifest also in proportion to the number of such groups. But the hypothesis that the dissociation of the hexa-arylethanes is proportional to the complexity of the aryl groups becomes wholly untenable when one compares triphenylmethyl with phenyl-

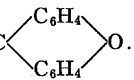
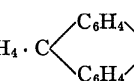
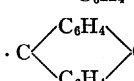
xanthyl, $\text{C}_6\text{H}_5\text{C}$ , which is monomolecular to the extent of

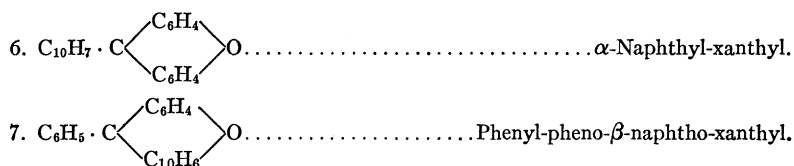
82%.⁹ Is the union of the two phenyl groups the paramount influence in this case? If so, why should a substance constitutionally so closely related to the xanthyls as phenyl-biphenylene-methyl,

$\text{C}_6\text{H}_5\text{C}$ , be completely dimolecular?¹⁰

It is obvious that from the few facts known to us at present it is difficult, if not wholly impossible, to formulate the relation between the complexity of the aryl groups in the hexa-arylethanes on the one hand and the tendency of these ethanes toward dissociation into free radicals on the other.

The Problem of this Investigation.—In order to obtain some further knowledge as to the factors governing the equilibrium between the di- and the mono-molecular phases of triarylmethyls, we decided to select for our study a related set of compounds. The following triarylmethyls were prepared for this purpose:

1. $(\text{C}_6\text{H}_5)_3\text{C}$ Triphenylmethyl.
2. $(\text{C}_6\text{H}_5)_2\text{C} \cdot \text{C}_{10}\text{H}_7$ α -Naphthyl-diphenylmethyl.
3. $\text{C}_6\text{H}_5 \cdot \text{C}$ ..... Phenyl-xanthyl.
4. $\text{CH}_3\text{C}_6\text{H}_4 \cdot \text{C}$ ..... *p*-Tolyl-xanthyl.
5. $\text{ClC}_6\text{H}_4 \cdot \text{C}$ ..... *p*-Chlorophenyl-xanthyl.



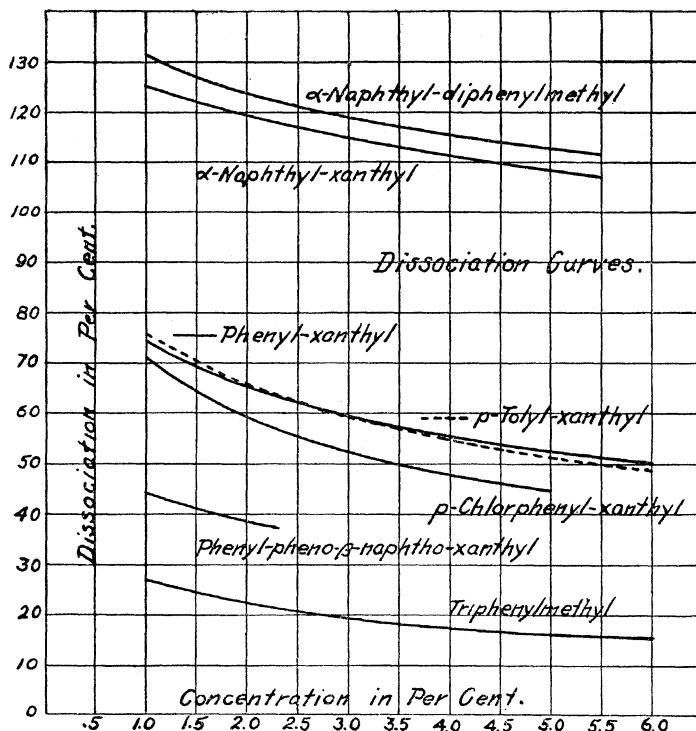
A determination of the molecular state, and consequently of the dissociation phenomenon, of these unsaturated compounds is the more pertinent in view of the limited number of radicals upon which such determinations have been conducted in the past. Further and, if possible, more certain evidence with respect to the dissociation of these hydrocarbons, and consequently with respect to the trivalency of carbon, is most desirable.

Our aim has been to take every possible precaution to insure uniformity and purity of the triarylmethyls to be used. As a check, the capacity for oxygen absorption and for peroxide formation was always resorted to, using part of the very same sample which served for the determination of the molecular weight. This is a very essential and one of the safest criterions for the purity of the products, the reaction being: $2 \text{R}_3\text{C} + \text{O}_2 = \text{R}_3\text{C}-\text{O}-\text{O}-\text{R}_3\text{C}$. Also it was made certain that during the course of the determination the triarylmethyl suffered no deleterious isomerization due to the effect of the temperature (80°) of the solvent, naphthalene. Each experiment represents an individual preparation and in no case were two determinations of the molecular weight made upon the same sample. Moreover, the sample was never more than one day old, the free radical being prepared in the afternoon, allowed to crystallize over night, isolated the following morning and the molecular weight taken the same afternoon. The molecular weight determinations themselves were carried out in an atmosphere of hydrogen, oxygen being completely excluded from the whole apparatus. The details regarding the preparation of the pure compounds and the method used in the molecular weight determinations will appear shortly in the *Journal of the American Chemical Society*.

The triarylmethyls were studied from two points of view. (1) The molecular weight of every triarylmethyl was determined within a fairly wide range of concentration, from 1% to 6%, in order to determine the effect of concentration upon the degree of dissociation. (2) From a comparison of the degree of dissociation of various triarylmethyls, under the same conditions of solvent, concentration and temperature, it was hoped that something would be learned regarding the

influence of the various aryl groups upon the tendency of the ethane towards dissociation.

Summary of the Results.—In the diagram are represented the curves, each curve based upon a number of molecular weight determinations, expressing the dissociation tendency of the hexa-arylethanes mentioned in this paper. The curves are plotted with the percentage of concentration as abscissas and the dissociation values, in percentages, as ordinates. The values expressing dissociation were



obtained according to the formula $x = \frac{M_t - M_o}{M_o}$, where x equals the degree of dissociation, M_t represents the theoretical molecular weight of the hexa-arylethane and M_o the molecular weight actually found.

1. In all instances, a steady and gradual increase of the molecular weight is noticeable as one proceeds from a 1% concentration of the radical to that of 6%. The generality of these results, and their uniformity, leave no room for doubt that we are dealing here with a phenomenon of molecular dissociation, wherein the products of dissociation are in equilibrium with the dissociating substance. An

equilibrium of this nature might be expected to shift in favor of dissociation with dilution, as is actually the case with these compounds.

2. When in triphenylmethyl two phenyl groups become joined through an oxygen atom and thus give rise to a xanthone ring, the tendency of the new compound, phenyl-xanthyl, towards dissociation increases to a marked extent, approximately threefold.

3. A phenyl and a *p*-tolyl group are apparently equivalent in their influence for dissociation when linked to a xanthone ring; a *p*-chlorophenyl group is of somewhat lesser influence, as can be seen on comparing the dissociation curves of the three corresponding aryl-xanthyls. This equality of influence of a *p*-tolyl and a phenyl group would not necessarily have been anticipated. Toly-diphenylmethyl differs very much from triphenylmethyl, and tri-*p*-tolylmethyl is so unstable that it is apparently impossible to isolate it, owing to the tendency to isomerize or polymerize.

4. An α -naphthyl group when replacing a phenyl group in triphenylmethyl exerts upon the dissociation equilibrium of the compound a very decided influence in favor of the monomolecular phase— α -naphthyl-diphenylmethyl appearing as wholly dissociated. This favorable influence of the naphthyl group is still retained when the group is linked to a xanthone ring, the resulting compound being also dissociated to the extent of 100%. And yet, when the naphthyl group enters as a component in the formation of the xanthone ring itself, it depresses very decidedly the dissociation tendency of the compound, as is evident on comparing the two isomers, α -naphthyl-xanthyl and phenyl-pheno- β -naphtho-xanthyl.

5. It has been established that the triarylmethyls are, in the solid state, almost wholly devoid of color, being, like triphenylmethyl itself, only pale-yellow; but their solutions differ very much, being yellow, orange, brown, red, or green, according to the individual compound. Schlenk has described tribiphenylmethyl, 100% dissociated, as a dark green powder. Whether this difference in color from our completely dissociable radicals is real or only apparent we cannot at present say. The fact that triarylmethyls, colorless when solid, give color only when in solution, lends support to the hypothesis that the triarylmethyls do undergo tautomerization when dissolved. Not dissociation alone into triarylmethyl, but, in addition thereto, the consequent tautomerization of this into its quinonoid modification, $R_2C = \text{C}_6\text{H}_4$, constitute a satisfactory explanation of the color phenomenon. Tautomerization commonly occurs, indeed,

only when the compound capable of tautomerization is in the liquid phase, or in solution. And that is just the case with the free radicals under consideration.

6. The two radicals, α -naphthyl-diphenylmethyl and α -naphthyl-xanthyl, were found to give a molecular weight *less* than that calculated for the monomolecular phase. Schlenk and Renning's¹¹ results show that α -naphthyl-biphenyl-phenylmethyl exhibits the same unusual behavior. We have good reasons to believe that our results are not due to experimental errors, and we took pains to verify them repeatedly. The cause of this unexpected result may possibly lie in a still further dissociation of the triarylmethyl itself, $R R' R'' C \rightleftharpoons R R' C + R''$.

¹ Gomberg, *Berlin, Ber. D. Chem. Ges.*, **40**, 1907, (1860); **42**, 1909, (406); Gomberg and Cone, *Liebigs Ann. Chem. Leipzig*, **370**, 1909, (190); **376**, 1910, (208).

² Gomberg, *Berlin, Ber. D. Chem. Ges.* (406); **46**, 1913, (228).

³ Compare G. N. Lewis, these PROCEEDINGS, **2**, 1916, (588).

⁴ Gomberg and Cone, *Berlin, Ber. D. Chem. Ges.*, **37**, 1904, (2037).

⁵ Schlenk and Mair, *Liebigs Ann. Chem., Leipzig*, **394**, 1912, (179).

⁶ Schmidlin, *Das Triphenylmethyl*, Stuttgart, 1914, (94).

⁷ Piccard, *Liebigs Ann. Chem., Leipzig*, **381**, 1911, (347).

⁸ Schlenk, *Ibid.*, **372**, 1909, (4); **394**, 1912, (186); *Berlin, Ber. D. chem. Ges.*, **43**, 1910, (1756); Schmidlin and Garcia-Banus, *Ibid.*, **45**, 1912, (3176).

⁹ Schlenk and Renning, *Liebigs, Ann. Chem., Leipzig*, **394**, 1912, (189).

¹⁰ Schlenk, Herzenstein and Weickel, *Berlin, Ber. D. chem. Ges.*, **43**, 1910, (1754).

¹¹ Schlenk and Renning, *Liebigs Ann. Chem., Leipzig*, **394**, 1912, (195).

SEX-DETERMINATION AND SEX-DIFFERENTIATION IN MAMMALS

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Read before the Academy, April 17, 1917

The principle of zygotic sex-determination is generally regarded as established for mammals as for other animal groups. The reasons for this are (1) the identity of sex of all individuals derived from a single zygote: e.g., identical twins, quadruplets of armadillos, etc.; (2) the facts of sex-linked inheritance, which demonstrate the inheritance of certain sex factors in a Mendelian way; (3) the dimorphism of spermatozoa in mammals as in other groups with zygotic determination of sex. We must therefore regard sex as *determined*, in the usual sense of the word, at the time of union of the gametes.

The question, however, arises, whether sex-determination involves an irreversible tendency to the corresponding sex-differentiation, or